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## EUROPEAN PATENT APPLICATION

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(71) Applicant: SECO TOOLS AB  
S-737 82 Fagersta (SE)

(72) Inventor: Ruppi, Sakari  
737 44 Fagersta (SE)

(74) Representative: Taquist, Lennart et al  
Sandvik AB  
Patents & Licences  
Fack  
811 81 Sandviken 1 (SE)

### (54) Deposition of gamma- $\text{Al}_2\text{O}_3$ by means of CVD

(57) There is disclosed a coated body having as the outer layer a layer of  $\gamma$ - $\text{Al}_2\text{O}_3$  deposited by chemical vapor deposition, preferably at a temperature of from 700-900°C.

The  $\gamma$ - $\text{Al}_2\text{O}_3$  layer is formed through the use of a gaseous mixture including  $\text{H}_2\text{S}$  in amounts significantly higher than those presently used and at a temperature of from 700-900°C. The method is also disclosed.

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**Description****BACKGROUND OF THE INVENTION**

5 [0001] Aluminum oxide (alumina,  $\text{Al}_2\text{O}_3$ ) exists in many metastable polymorphs such as  $\gamma$ ,  $\eta$ ,  $\theta$ ,  $\delta$ ,  $\kappa$ , and  $\chi$  in addition to the thermodynamically stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase (corundum). When produced by chemical vapor deposition (CVD),  $\text{Al}_2\text{O}_3$  crystallizes into  $\kappa$ - $\text{Al}_2\text{O}_3$  and  $\theta$ - $\text{Al}_2\text{O}_3$  modifications in addition to the stable  $\alpha$ - $\text{Al}_2\text{O}_3$ . Earlier CVD coatings were usually mixtures of several polymorphs, the most commonly occurring metastable  $\text{Al}_2\text{O}_3$  modification being  $\kappa$ - $\text{Al}_2\text{O}_3$ . Today, both  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\kappa$ - $\text{Al}_2\text{O}_3$  polymorphs are used as hard coatings, and they can be deposited in a controlled way by modern CVD technology shown, for example in U.S. Patents 5,137,774 and 5,700,569.

10 [0002] Dopants of hydrogen sulfide ( $\text{H}_2\text{S}$ ), phosphorus chloride ( $\text{PCl}_3$ ) carbonoxysulfide (COS) or phosphine ( $\text{PH}_3$ ) can be applied in order to increase the growth rate and thickness uniformity of the alumina layers. The most commonly applied dopant is  $\text{H}_2\text{S}$  as also disclosed in U.S. Patent 4,619,886. While amounts of  $\text{H}_2\text{S}$  in the total CVD gaseous mixture of from 0.003 to 1% by volume and temperatures of 700 to 1200°C are broadly disclosed in that patent, all 15 exemplifications of the process therein are below 0.5 vol % and generally around 0.1 to 0.3 vol %  $\text{H}_2\text{S}$  used at temperatures of 1000-1030°C.  $\text{H}_2\text{S}$  has been called the "magical dopant" in view of its effect on improving the growth rate and uniformity of  $\text{Al}_2\text{O}_3$  coatings applied by conventional CVD techniques at temperatures around 980°C. See, Oshika et al., "Unveiling the Magic of  $\text{H}_2\text{S}$  on the CVD- $\text{Al}_2\text{O}_3$  Coating", J. Phys IV France 9 (1999), Pr 8-877-Pr 8-883.

20 [0003] CVD  $\kappa$ - $\text{Al}_2\text{O}_3$  is considered to exhibit morphological advantages (smaller grain size and lower porosity), lower thermal conductivity and even a higher hardness when compared with the CVD  $\alpha$ - $\text{Al}_2\text{O}_3$  phase. These are important properties when metal cutting is concerned. However, at the relatively high temperatures (> 1000°C) reached during metal cutting, metastable  $\kappa$ - $\text{Al}_2\text{O}_3$  may transform to the stable  $\alpha$ - $\text{Al}_2\text{O}_3$  polymorph.  $\gamma$ - $\text{Al}_2\text{O}_3$ , when deposited using physical vapor deposition (PVD) or plasma assisted CVD has been found to exhibit high hardness and good wear properties. See, for example, WO 9924634 and U.S. Patent No. 5,879,823. However,  $\gamma$ - $\text{Al}_2\text{O}_3$  has not been available 25 using conventional CVD techniques.

**OBJECTS AND SUMMARY OF THE INVENTION**

30 [0004] It is an object of this invention to avoid or alleviate the problems of the prior art.

[0005] It is further an object of this invention to provide  $\gamma$ - $\text{Al}_2\text{O}_3$  using conventional CVD.

35 [0006] In one aspect of the invention there is provided a coated body having as the outer layer, a layer of  $\gamma$ - $\text{Al}_2\text{O}_3$  deposited by chemical vapor deposition.

[0007] In another aspect of the invention there is provided a method of forming a coated body having a layer of  $\gamma$ - $\text{Al}_2\text{O}_3$  comprising coating the body with a gaseous mixture of  $\text{AlCl}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{S}$  at a temperature of from about 40 600 to 800°C, the  $\text{H}_2\text{S}$  being present in amounts of at least 0.7% of the total mixture.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0008] The Figure is a graph of growth rates of  $\kappa$  and  $\gamma$ - $\text{Al}_2\text{O}_3$  at varying temperatures and amounts of  $\text{H}_2\text{S}$  in the 40 gaseous coating mixture.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION**

45 [0009] It has hitherto been thought that  $\gamma$ - $\text{Al}_2\text{O}_3$  can only be obtained by plasma assisted CVD or PVD processes. It has now surprisingly been found that  $\gamma$ - $\text{Al}_2\text{O}_3$  can be obtained by using conventional CVD under specific circumstances discussed below.

50 [0010] Growth rates of  $\alpha$ -alumina vs.  $\text{H}_2\text{S}$  content at 1000°C and 800°C are shown in The Figure. An important observation is that at 800°C, reasonably high growth rates could be obtained. The most important observation, however, is that at higher  $\text{H}_2\text{S}$  contents,  $\gamma$ - $\text{Al}_2\text{O}_3$  was obtained. At 800°C  $\gamma$ - $\text{Al}_2\text{O}_3$  could be obtained at  $\text{H}_2\text{S}$  contents of 0.75-1.7% by volume of the total gaseous mixture, preferably greater than 1 vol %, and at a pressure of 100 mbar. At 1000°C, regardless of the amounts of  $\text{H}_2\text{S}$ ,  $\kappa$ - $\text{Al}_2\text{O}_3$  is always formed. Thus, by carefully controlling the amount of  $\text{H}_2\text{S}$  and the temperature of the application, the preferred polymorph,  $\gamma$ -alumina, can surprisingly be formed. When studied using TEM (transmission electron microscopy),  $\gamma$ - $\text{Al}_2\text{O}_3$  exhibited a very high defect density and obviously a high hardness.

55 [0011] The product of the present invention may be made utilizing conventional CVD techniques and apparatus, using, however, a greater amount of  $\text{H}_2\text{S}$  than conventionally used in CVD processes and a higher pressure.  $\text{H}_2\text{S}$  is added in amounts greater than 0.7 vol %, generally 0.75 to 1.7 vol %, preferably greater than 1 up to about 1.5 vol %, of the total gaseous mixture. The amounts of the other reactants can be adjusted accordingly but usually the alumina formers, an aluminum halide and an oxidizing gas (e.g., water vapor formed by the reaction of  $\text{CO}_2$  and/or  $\text{CO}$  and  $\text{H}_2$ )

are maintained as before and the amount of reducing agent (excess H<sub>2</sub>) is reduced.

[0012] The coating process is performed at temperatures of from about 700 to 900°C, preferably 750 to 850°C, at a pressure of from about 50 to 600 mbar, preferably from about 100 to 300 mbar, for a time sufficient to form the coating, generally from about 2 to 10 hours, preferably from about 4 to 8 hours.

5 [0013] The resulting coating is from about 1.0 to 5 µm, preferably from about 2 to 4 µm, in thickness.

[0014] The body on which the γ-Al<sub>2</sub>O<sub>3</sub> layer is applied can be a cemented carbide, ceramic, cermet (for metal cutting purposes) or steel (for catalysis). These bodies are well-known in the art and any such conventional material may be used.

10 [0015] The γ-Al<sub>2</sub>O<sub>3</sub> layer may be applied as the outermost or as an inner layer. When used as the outermost layer, the γ-Al<sub>2</sub>O<sub>3</sub> layer may be applied onto an Al<sub>2</sub>O<sub>3</sub> layer, which itself can be applied onto one or more other layers such as, for example, TiC and (Ti,Al)N. The Al<sub>2</sub>O<sub>3</sub> layer can be an alpha phase, a kappa phase or a mixture of alpha and kappa phase Al<sub>2</sub>O<sub>3</sub>. The γ-Al<sub>2</sub>O<sub>3</sub> layer may also be applied onto a TiN, Ti(C,N) or (Ti,Al)N layer.

[0016] Similarly, when the γ-Al<sub>2</sub>O<sub>3</sub> layer is applied as an inner layer, there may be other layers such as Al<sub>2</sub>O<sub>3</sub>, TiC, Ti(C,N), TiN or the like applied atop the γ-Al<sub>2</sub>O<sub>3</sub> layer.

15 [0017] These various inner and/or outer layers may be applied by CVD, MTCVD or PVD.

[0018] The invention is additionally illustrated in connection with the following Examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

## 20 Example 1

[0019] A single layer of γ-Al<sub>2</sub>O<sub>3</sub> was deposited using the following process data on a Ti(C,N) layer having a thickness of 3 µm:

25 T = 800°C

H<sub>2</sub>S = 1%

AlCl<sub>3</sub> = 2.5%

CO<sub>2</sub> = 5.0%

H<sub>2</sub> = balance

30 Pressure (P) = 100 mbar

Deposition time is 6 hours

[0020] A coating composed of γ-Al<sub>2</sub>O<sub>3</sub> was obtained. The same coating was also deposited atop PVD TiN, Ti(C,N) and (Ti,Al)N layers with a thickness of 3 µm. Further, CVD coatings of κ-Al<sub>2</sub>O<sub>3</sub> and α-Al<sub>2</sub>O<sub>3</sub> were deposited on the PVD layers as well as CVD layers for comparative tests dealt with later on.

### Hardness of γ-Al<sub>2</sub>O<sub>3</sub>:

#### [0021]

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Alumina Phase	Hardness
γ-Al <sub>2</sub> O <sub>3</sub>	23 GPa
α-Al <sub>2</sub> O <sub>3</sub>	20 GPa
κ-Al <sub>2</sub> O <sub>3</sub>	21 GPa

### Orientation Relationships

50 [0022] The single layers of γ-Al<sub>2</sub>O<sub>3</sub> were deposited using the following process data on a PVD TiN, Ti(C,N) and (Ti,Al)N layers having a thickness of 3 µm:

T = 700°C

H<sub>2</sub>S = 1.6%

AlCl<sub>3</sub> = 2.5%

CO<sub>2</sub> = 7.0%

H<sub>2</sub> = balance

P = 100 mbar

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Deposition time is 8 hours

TEM micrographs of the PVD TiN- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> interface confirmed the following orientation relationship between PVD TiN and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:

5           (111)<sub>PVD-TiN</sub> // (111) <sub>$\gamma$</sub>   
              [110]<sub>PVD-TiN</sub> // [110] <sub>$\gamma$</sub>

[0023] This orientation relationship is valid for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-PVD TiN, Ti(C,N) or (Ti,Al)N in general and is naturally not dependent on which technique (PVD or CVD) is used to deposit  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The orientation relationship describes in  
10 general epitaxy between a face-centered cubic (fcc, preferably fcc B1) coating (TiN, Ti(C,N), (Ti,Al)N) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (cubic spinel structure).

[0024] Cutting performance in turning of Stainless Steel 1672:

Cutting Speed: 200 m/min  
 15 Feed: 0.4 mm/r  
 Depth of Cut: 2.0 mm  
 Insert Style: CNMG 120408-M3  
 Coolant: No

20

Coating (thickness 3 $\mu$ m on TiCN coating)	Average life time/min
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	9.8
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	6.5
$\kappa$ -Al <sub>2</sub> O <sub>3</sub>	9.6

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[0025] Edge strength /chipping resistance of alumina polymorphs

Turning against shoulder

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Cutting Speed: 200 m/min  
 Feed: 0.4 mm/r  
 Depth of Cut: 2.0 mm  
 Insert Style: CNMG 120408-M3  
 Coolant: No

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Coating (thickness 3 $\mu$ m on TiCN + 3 $\mu$ m Al <sub>2</sub> O <sub>3</sub> )	Edge chipping after 2 min
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	10%
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	15%
$\kappa$ -Al <sub>2</sub> O <sub>3</sub>	10%

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[0026] Edge strength/chipping resistance in milling SS2244

[0027] The chipping resistance of PVD TiN, Ti(C,N) and (Ti,Al)N coatings with and without an alumina top layer were studied.

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Cutting Speed: 220 m/min  
 Feed: 0.2 mm/tooth  
 Depth of Cut: 2.5 mm  
 Insert Style: SEKN1203

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Coating	Thickness	Chipping after 600 mm	Performance/mm
PVD TiN	3	5%	3660
PVD Ti(C,N)	3	5%	4200

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(continued)

	Coating	Thickness	Chipping after 600 mm	Performance/mm
5	PVD (Ti,Al)N	3	5%	4600
	PVD TiN	6	10%	4700
	PVD Ti(C,N)	6	10%	5100
	PVD (Ti,Al)N	6	10%	6800
10	PVD Ti(C,N)- $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	3+3	10%	7200
	PVD Ti(C,N)- $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3+3	30%	7100
	PVD Ti(C,N)- $\kappa$ -Al <sub>2</sub> O <sub>3</sub>	3+3	25%	5100

15 [0028] It is obvious that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which can be deposited at lower temperatures than the other CVD alumina phases did not anneal out the compressive stresses in the PVD layers resulting in the better edge strength.

20 [0029] The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

### Claims

25 1. A coated body having as the outer layer, a layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> deposited by chemical vapor deposition.

2. The coated body of claim 1 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer is deposited at a temperature of from about 700 to 900°C.

3. The coated body of claim 1 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer is deposited on one or more layers taken from the group consisting of TiC, TiN, Ti(C,N), (Ti,Al)N and Al<sub>2</sub>O<sub>3</sub>.

30 4. The coated body of claim 3 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer is deposited upon one or more layers of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\kappa$ -Al<sub>2</sub>O<sub>3</sub> or mixtures thereof.

5. The coated body of claim 3 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer is deposited upon a (Ti,Al)N layer.

35 6. The coated body of claim 1 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer is deposited on a layer which has been deposited by physical vapor deposition.

7. The coated body of claim 6 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is deposited on one or more of TiC, TiN, Ti(C,N) and (Ti,Al)N.

40 8. The coated body of claim 1 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is deposited on a layer having a face-centered cubic structure.

9. The coated body of claim 8 wherein the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has an orientation relationship with the layer having a face-centered cubic structure (fcc) of

(111)<sub>PVD-fcc</sub> // (111) <sub>$\gamma$</sub>   
[110]<sub>PVD-fcc</sub> // [110] <sub>$\gamma$</sub>

45 50 10. The coated body of claim 9 wherein the layer having a face-centered cubic structure is taken from the group consisting of TiN, TiC, Ti(C,N), (Ti,Al)N and mixtures thereof.

11. The coated body of claim 10 wherein the layer having a face-centered cubic structure is a fcc B1 structure deposited by CVD technique.

55 12. The coated body of claim 10 wherein the layer having a face-centered cubic structure is a fcc B1 structure deposited by PVD technique.

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13. The coated body of claim 1 wherein the body is composed of a cemented carbide, cermet, ceramic or steel.
14. The coated body of claim 13 wherein the body is a cemented carbide.
- 5 15. A method of forming a coated body having a layer of  $\gamma\text{-Al}_2\text{O}_3$  comprising coating the body with a gaseous mixture of  $\text{AlCl}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{S}$  at a temperature of from about 700 to 900°C, the  $\text{H}_2\text{S}$  being present in amounts of at least 0.7% of the total mixture.
- 10 16. The method of claim 15 wherein the coating is conducted at a temperature of from about 750 to 850°C.
17. The method of claim 15 wherein the coating is conducted at a pressure of from about 100 to 500 mbar.
18. The method of claim 15 wherein the body being coated is a ceramic, cermet, cemented carbide or steel.
- 15 19. The method of claim 18 wherein the body being coated contains at least one other layer of TiC, TiN, Ti(C,N), TiAlN or  $\text{Al}_2\text{O}_3$ .
20. The method of claim 19 wherein the said other layer is applied by physical vapor deposition.

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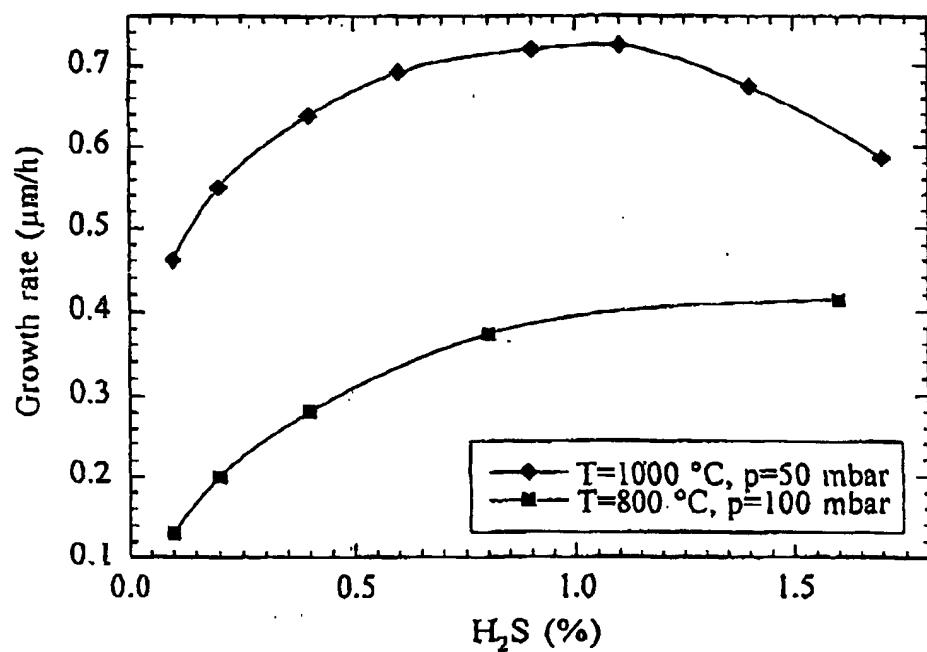
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EP 01 85 0020

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<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>23 May 2001</td> <td>Ekhult, H</td> </tr> </table>				Place of search	Date of completion of the search	Examiner	THE HAGUE	23 May 2001	Ekhult, H
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